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13. ABSTRACT (Maximum 200 words)

c-axis oriented HTSC films were grown by LPE on varius substrates. The conditions for improving the surface flatness were systematically studied. For the achievement of interstep distances $y_o \approx 10\mu m$ between monosteps of 12Å, as required for Tunnel devices, following requirements were estimated : undercooling $\Delta T \approx 0.17K$, misfit $\leq 0.08\%$, substrate misorientation $\leq 0.02°$. The defect structure and morphology of LPE films was investigated. For YBCO on (110) NGO, at growth temperature, the epitaxial strain induced by misfit can be released by misfit dislocations MD already in the first few monolayers. During cooling/oxidation, the formation of {110} twins partially relax the strain. The remaining effective strain is accomodated by crack formation. The orientational relationship between twinning/cracking related to the misfit was studied and cdritical thicknesses for the formation of MD and of cracks were estimated. High-quality LPE films could not be obtained on LSAT substrates, whereas same growth conditions yielded good-quality LPE films on NGO. This might be due to the striations present in LSAT which may influence nucleation and growth behavior. Solid-solutions of substrates and of HTSC allow to reduce misfit problems during growth but still the cooling/oxidation problem and lead to twinning and cracking.

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High-quality c-axis oriented HTSC Films for Microwave Devices

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Contractor : Prof. F.-K. Reinhart / Dr. Hans J. Scheel

Contract Number : N68171-96-C-9105

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Introduction

The objective of this seed project was to grow by liquid-phase epitaxy (LPE) extremely flat HTSC layers displaying very little cracking. This required the systematic study of several aspects.
The flattest surfaces are expected from the Frank van der Merwe FVM (layer-by-layer) growth mode, which is only possible under very low supersaturation conditions, which requires an accordingly precise supersaturation control. Under near-equilibrium conditions (LPE-growth), the substrate parameters misfit, misorientation, chemical stability set the limits of the achievable film morphology. Thus, they were extensively studied in this work. Many parameters could be estimated from the experiments, and compared with existing theories. This allows to adjust the growth parameters for improved film quality.

1) Supersaturation control

The FVM growth mode can only be achieved under very low supersaturation conditions **[1]**, by using LPE. The adjustment of the supersaturation requires the knowledge/study of the primary crystallization field and solubility of the concerned compounds. Thus, the solubility of YBCO and NdBCO in the BaO/CuO flux containing 30mol% and 31mol% BaO was determined experimentally **[2,3]**, and the heat of solution of both compounds derived **[3]**. By using the Cabrera-Levine CL **[4]** theory and our solubility data, this allows to estimate the supersaturation from growth features (spirals) on c-axis oriented LPE YBCO films **[5]**. From this, the supersaturation σ required for the achievement of interstep distances $y_o \approx 10\mu m$ between monosteps of 12Å was estimated at $\sigma \approx 0.17°C$ **[5]**.
In our system, for our growth conditions, the orientation of YBCO films on (110) $NdGaO_3$ (NGO) could be chosen by adjusting the supersaturation : at $\sigma \leq 3K$, c-axis oriented films are obtained, whereas at $\sigma \geq 3K$ a-oriented films are grown. This a-/c-orientation transition in LPE depends also on the flux composition. Thus, the results presented here are valid for our growth system/conditions. On (001) NGO, c-oriented films are generally obtained.

2) Misfit-related problems

For the growth of extremely flat surfaces under near equilibrium conditions, the substrate has to fulfill severe requirements. Besides high chemical stability in the highly corrosive flux, the maximum tolerable misfit between substrate and film was theoretically estimated at $\leq 0.1\%$ **[6]**, and the substrate misorientation smaller than 0.1°. From our experimental results of YBCO on (110) NGO **[7]**, and precision high-temperature X-ray diffraction lattice constants determinations **[8]**, we could estimate these parameters more precisely. Accordingly, for the achievement of interstep distances of about 10μm between monosteps of 12Å for c-oriented YBCO films, the

maximum tolerable misfit would be 0.08%, and the substrate misorientation should not exceed about 0.02° in order to avoid step bunching. From this, it follows that for c-oriented YBCO films of (110) NGO, monospirals having a maximum interstep distance of about 2.5μm can be grown.
An attempt was made to use LSAT substrates (solid solution of $0.3LaAlO_3$-$0.7Sr_2AlTaO_6$) supplied by Dr. S. Tidrow and others bought from a company. The growth morphology of these YBCO LPE layers was atypical, dendrite-like, also for the layers grown at very low supersaturation. Therefore, simultaneous dipping of a NGO and a LSAT substrate was done. Whereas an epitaxial layer was obtained on NGO, no epitaxy could be observed on the LSAT substrate. The striations of these LSAT substrates, which can easily be observed under the microscope, may have an influence on the nucleation and growth behavior, especially in the case of growth under near-equilibrium conditions. An alternative approach would be to deposit a YBCO buffer-layer by vapor-growth onto the LSAT substrates prior to LPE. However, the expected low quality of the buffer layer would probably not allow the overgrowth of a high-quality YBCO film by LPE.
In order to suppress and understand the misfit problems we have studied solid solutions of substrates and of HTSC films. These may reduce misfit problems during growth [9] but still the cooling/oxidation problems remain and lead to twinning and cracking.

3) Corrosion problems

The precise adjustment of supersaturation requires a homogeneous and constant chemical composition of the flux. The corrosion of the crucible walls lead to a time- and temperature-dependent shift of either the solubility or supersaturation [Solubility]. The first case applies to ZrO_2 crucibles, where the $BaZrO_3$ formation near the crucible wall shifts the Ba:Cu-ratio of the solution, and the second case applies to Y2O3 crucibles, where the continuous supply of yttrium from the crucible wall lead to a self-saturation system. In this case, supersaturation could be nevertheless achieved by using step-cooling instead of ramp-cooling.
Not only the crucibles, but also the substrates are attacked by the highly corrosive flux. In the case of YBCO on NGO, the required small supersaturation of 0.17K cannot be set. In order to obtain larger interstep distances, as required for tunnel device applications [5], the supersaturation was systematically reduced (from 3K on). We observed in this case only a-axis growth. For short growth times of about 2 min., the morphology of such a-layers appeared squamous. We suppose that if the supersaturation is too small to compensate the misfit/strain effects, the substrate is attacked. NdBCO has a higher thermal stability than YBCO (about 100°C higher) [3] and forms solid-solutions with YBCO. Therefore, the dissolved Nd^{3+} ions are incorporated at the interface by forming (Y,Nd)BCO, and this increases the supersaturation at the interface in such a way that the kinetically favoured a-axis growth occurs.

4) Stoichiometry problems

Besides YBCO, solid-solutions of (Y,Nd)BCO, SmBCO and NdBCO were also considered [9], and LPE experiments done. Unlike the widely studied Y-Ba-Cu-O system, Nd-Ba-Cu-O exhibits a solid solution $Nd_{1+x}Ba_{2-x}Cu_3O_{7\pm d}$, for $0.04 \leq x \leq 0.6$ [10].

In solution growth, the crystal composition is fixed by the growth conditions. Among others, the parameters which have an influence on the Nd:Ba ratio of the NdBCO crystals are the growth atmosphere (oxygen partial pressure) and the composition of the solution (Ba:Cu ratio).
Inductively coupled plasma emission spectroscopy (ICP) analysis was performed for the determination of the composition of NdBCO crystals **[11]** and LPE layers grown on (001) $NdGaO_3$. For comparison, ICP analysis was also performed on NdBCO platelet-crystals grown from Al_2O_3 crucibles. The high-purity starting chemicals CuO (5N) and Nd_2O_3 (4N) did not contain measurable (ICP analysis) cation impurities. In BaO_2, the main impurity is Sr, which is incorporated into the NdBCO lattice on Ba-sites. For the NdBCO crystals grown in Nd_2O_3 crucibles a composition of $Nd_{1.1}Ba_{1.8}Sr_{0.1}Cu_3O_{7-d}$ was found. For the NdBCO crystals and LPE layers grown in alumina crucibles, aluminum is incorporated at Cu-sites, and their composition was $Nd_{1.1}Ba_{1.8}Sr_{0.1}Cu_{2.5}Al_{0.5}O_{7+d}$.
In $Nd_{1+x}Ba_{2-x}Cu_3O_{7\pm d}$, the superconducting properties decrease nonlinearly with increasing x **[10]**. The variability of the critical transition temperatureT_c as a function of x and heat/oxidation treatments can be explained by the number of four-fold coordinated Cu atoms on the chains which can be varied by differing the amounts of paired and unpaired Nd^{3+} substituing for Ba^{2+}, resulting in partial charge transfer from the planes to the chains. For $0.04 \leq x \leq 0.3$, the superconducting transitions are sharp [10]. AC-susceptibility measurements on the NdBCO crystals, with composition $Nd_{1.1}Ba_{1.8}Sr_{0.1}Cu_3O_{7-d}$ yield a sharp transition at about $T_c \approx 77K$ **[11]**. This low T_c is due to the deviation from 1-2-3 stoichiometry, whereas the substituted Sr at Ba-sites seemed to have no influence.
Despite promising first results in surface flatness, due to the difficulties of stoichiometry control and related degradation of HTSC properties, the SmBCO and NdBCO and solid-solutions approaches were not further investigated so far.

5) Film morphology and defect structure

The surface morphology and defect structure **[12,13]** of the LPE films was studied by Nomarski interference differential contrast microscopy, atomic force microscopy AFM, and scanning tunelling microscopy STM.
At growth temperature, the epitaxial strain induced by misfit can be partially or completely released by the formation of misfit dislocations. Cracking does not occur if an optimum density of misfit dislocations with sufficient mobility can be generated. For a-oriented and c-oriented YBCO films on NGO, we obtain a critical thickness for the formation of misfit dislocations of 2nm and 20nm, respectively **[13, 14]**. Thus, the strain can be accomodated during LPE growth already in the first few monolayers.
When the grown LPE films are brought to room temperature, they are partially oxidized unless they are cooled in nitrogen atmosphere. The films have then to be annealed in oxygen to become superconducting. During this oxidation, the phase transition from tetragonal to orthorhombic and the splitting of the a- and b- axes leads to the formation of {110} twins which partially relax the strain. The remaining effective strain is accomodated by crack formation.
We measured film thicknesses and distances between the cracks for a- and c-oriented films on (110) NGO, and compared the results with the theory **[13]**. a-oriented YBCO LPE films grown on (110) NGO have the largest misfit of 2.6% for

$[001]_{film} \| [110]_{substrate}$. For this direction, during cooling from 1'000°C to room temperature, the strain cannot be relaxed by the formation of twins, and parallel cracks develop. The estimated effective strain is 1.8%. Twinning occurs in the other direction $[100]/[010]_{film} \| [001]_{substrate}$, in which generally no cracks are observed.
c-oriented YBCO LPE films grown on (110) NGO present a cross-hatch {110} twin pattern, which is very effective to relieve the strain. Thus, the measured crack distances are larger than expected, and the effective strain would be $\varepsilon \approx 0.08$.

Conclusion

Many problems of this complex system have been studied along this work. From the estimated parameters, the severe requirements became clearer. One of the major problems to be solved is the oxidation of the films without cracking.
The highly anisotropic oxygen diffusion along the crystal axis lead to a gradient of oxygen concentration in the film, and twin formation. Thus, the films are inequally strained along their depth (and length) during oxidation. Highly perfect LPE films are difficult to oxidize, since oxidation is more efficient along defects. Theoretical calculations would be required in order to establish the optimal oxidation/cooling procedure, in order to obtain high-quality crack-free films.

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[3] C. Klemenz and H. J. Scheel, "Solubility of $YBa_2Cu_3O_{7-d}$ and $Nd_{1+x}Ba_{2-x}Cu_3O_{7\pm\delta}$ in the BaO/CuO flux", J. Crystal Growth 200 (1999) 435.
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[12] C. Klemenz, "Hollow cores and step bunching effects on (001) YBCO surfaces grown by liquid-phase epitaxy", J. Crystal Growth 187 (1998) 221.
[13] C. Klemenz, I. Utke and H. J. Scheel, "Defects on YBCO films grown by liquid-phase epitaxy on NdGaO3", J. Crystal Growth, accepted.
[14] I. Utke, C. Klemenz and H. J. Scheel, in preparation.

Summary of most important results/estimated parameters

1) The heat of solution of YBCO in the BaO/CuO-flux at 31mole% BaO (in air) and 1000°C is 34.7kcal/mol.

2) The heat of solution of NdBCO in the same flux is 28.1kcal/mol at 1060°C.

3) A supersaturation $\sigma < 0.017$, corresponding to an undercooling of < 0.17°C, has to be adjusted for the achievement of flat, c-axis oriented YBCO films with interstep distances $y_o \geq 10\mu m$ between monosteps of 12Å .

4) Due to the highly corrosive melt and due to the low supersaturation, a high chemical stability of the substrate is required.

5) A small supersaturation of 0.17°C cannot be set for $NdGaO_3$ substrates, due to etch-back and regrowth problem (formation of (Y,Nd)BCO, i.e. subsequent increase of supersaturation at the interface, leading to a change in the layer orientation).

6) For YBCO on (110) $NdGaO_3$ the roughness parameters are $\alpha_{(001)} \approx 13.25$ (c-films) and $\alpha_{(100)} \approx 9.96$ (a-films).

7) For the achievement of interstep distances of about 10μm, the maximum tolerable misfit is $f \leq 0.08\%$ at growth temperature of 1000°C. Thus, for c-YBCO films on (110) $NdGaO_3$, monospirals with a maximum interstep distance of $y_o \approx 2.5\mu m$ ($\rho_c \approx 130nm$) can be grown.

8) The substrate misorientation should be ≤ 0.02° to avoid step-bunching.

9) The critical thickness h_c for strain accommodation by misfit dilocations is $h_c \approx 2nm$ and $h_c \approx 20nm$ for a- and c-oriented fims, respectively, and critical thicknesses for cracks are 100nm and 1μm for a- and c-oriented films, respectively. Therefore, strain accomodation proceeds first by misfit dislocations formation, whereas cracking occurs during cooling and oxidation.

10) c-YBCO films on $NdGaO_3$ thicker than 500nm cannot be cooled down to room temperature without cracking in a non-oxidizing atmosphere, since the effective strain generated by the angular misfit is 0.8%, and a twinned c-YBCO layer, formed by in-situ oxidation, will crack directly after epitaxy if its thickness is larger than 500nm.

11) For LPE-grown YBCO films on (110) $NdGaO_3$, there seems to exist a maximum growth rate of ≈ 1.745μm/min.

12) The driving force for epitaxy from the vapor is estimated to be about $\Delta G \approx$ 37'000J/mol, whereas for an undercooling of 2.5K in LPE, the driving force for epitaxy, $\Delta G_{(\Delta T=2.5)} \approx 285$J/mol is obtained.

List of recent publications

1) C. Klemenz and H. J. Scheel, "Flat $YBa_2Cu_3O_{7-x}$ layers for planar tunnel-device technology", Physica C 265 (1996) 126-134.

2) M. Mukaida, S. Myazawa, C. Klemenz and H. J. Scheel, "Structural characterization of a-axis oriented $YBa_2Cu_3O_x$ films grown by liquid-phase epitaxy", J. Crystal Growth 169 (1996) 715-721.

3) I. Utke, C. Klemenz, H. J. Scheel, P. Nüesch, "High-temperature X-ray measurements of gallates and cuprates", J. Crystal Growth 174 (1997) 813-820.

4) I. Utke, C. Klemenz, H. J. Scheel, M. Sasaura, S. Myazawa, "Misfit problems in epitaxy of high-Tc superconductors", J. Crystal Growth 174 (1997) 806-812.

5) C. Klemenz, "Hollow cores and step bunching effects on (001) YBCO surfaces grown by liquid-phase epitaxy", J. Crystal Growth 187 (1998) 221.

6) C. Klemenz, I. Utke and H. J. Scheel, "Film orientation, growth parameters and growth modes in epitaxy of $YBa_2Cu_3O_{7-\delta}$" J. Crystal Growth, 1999, accepted.

7) C. Klemenz and H. J. Scheel, "Solubility of $YBa_2Cu_3O_{7-\delta}$ and $Nd_{1+x}Ba_{2-x}Cu_3O_{7\pm\delta}$ in the BaO/CuO flux", J. Crystal Growth 200 (1999) 435.

8) C. Klemenz and H. J. Scheel, "Growth and properties of $Nd_{1+x}Ba_{2-x}Cu_3O_{7\pm\delta}$ whiskers and needle-like crystals", J. Crystal Growth 203/4 (1999) 534.

9) C. Klemenz, I. Utke and H. J. Scheel, "Defects on YBCO films grown by liquid-phase epitaxy on NdGaO3", J. Crystal Growth, 1999, accepted.

Advanced degree earned

The PI, Eng. C. Klemenz submitted a PhD thesis at the University of Tokyo.
The title of the thesis : "Liquid Phase Epitaxy of YBCO and NdBCO High-temperature Superconductors", in print.
A final examination is foreseen end of 1999, with obtention of the degree of Doctor of Engineering of the University of Tokyo.